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(21)Application number : 2001-369340 (71)Applicant : TOKYO OHKA KOGYO CO LTD

(22)Date of filing : 03.12.2001 (72)Inventor : HANEDA HIDEO
FUJIMURA SATOSHI
IWASHITA ATSUSHI

(54) POSITIVE RESIST COMPOSITION AND RESIST PATTERN FORMING METHOD

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a chemically amplified positive resist composition excellent in resolution, capable of increasing the focal depth range of an isolated resist pattern and capable of suppressing a proximity effect.

SOLUTION: The positive resist composition is obtained by dissolving a resin component (A) having units derived from (meth)acrylic esters in the principal chain and having alkali solubility increased by the action of an acid and an acid generator component (B) which generates an acid upon exposure in an organic solvent (C). The resin component (A) is a copolymer comprising a unit (a1) derived from a (meth)acrylic ester containing a polycyclic group- containing acid-dissociable dissolution inhibiting group, a unit (a2) derived from a (meth)acrylic ester containing a lactone-containing monocyclic or polycyclic group, a unit (a3) derived from a (meth)acrylic ester containing a hydroxyl-containing polycyclic group and a unit (a4) derived from a (meth)acrylic ester containing a polycyclic group, other than the units (a1)-(a3).

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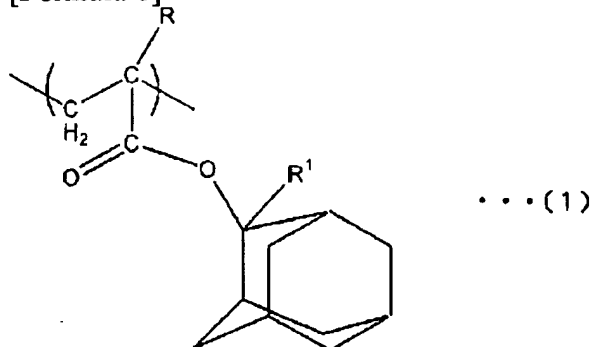
CLAIMS

[Claim(s)]

[Claim 1] The resinous principle to which it has the unit guided from acrylic ester in a principal chain, and the solubility over alkali increases according to an operation of an acid (A), (Meta) It is the positive-resist constituent which comes to dissolve the acid generator component (B) which generates an acid by exposure in an organic solvent (C). The unit guided from the acrylic ester in which a resinous principle (A) contains a polycyclic type machine content acid dissociation nature dissolution control radical (meta) (a1), The unit guided from the acrylic ester containing a lactone content monocycle or a polycyclic type machine (meta) (a2), The unit guided from the acrylic ester containing a hydroxyl-group content polycyclic type machine (meta) (a3), And the positive-resist constituent characterized by being a copolymer including the unit (a4) guided from the acrylic ester containing polycyclic type machines (meta) other than these units (a1), a unit (a2), and a unit (a3).

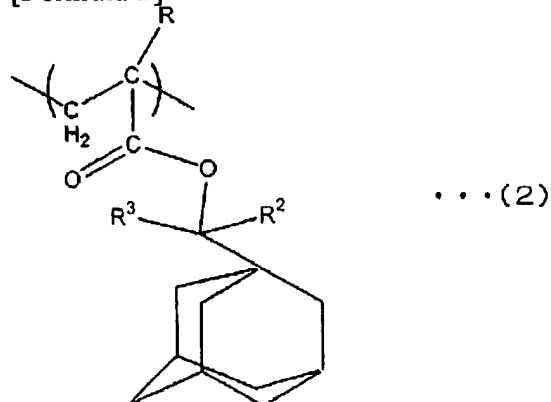
[Claim 2] The positive-resist constituent according to claim 1 whose unit (a1) is at least one sort chosen from what is expressed with the following general formula (1), (2), and (3).

[Formula 1]



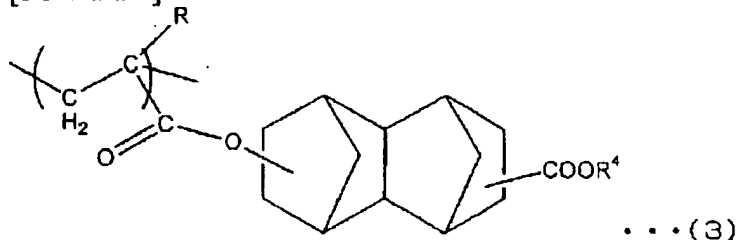
(For the inside R of a formula, a hydrogen atom or a low-grade alkyl group, and R1 are low-grade alkyl groups)

[Formula 2]



(For the inside R of a formula, a hydrogen atom or a low-grade alkyl group, R2, and R3 are the independent low-grade alkyl groups, respectively)

[Formula 3]



(For the inside R of a formula, a hydrogen atom or a low-grade alkyl group, and R4 are the 3rd class alkyl groups)

[Claim 3] A unit (a1) is expressed with the aforementioned general formula (1), and it is R1 in this general formula (1). Positive-resist constituent according to claim 2 which is a methyl group.

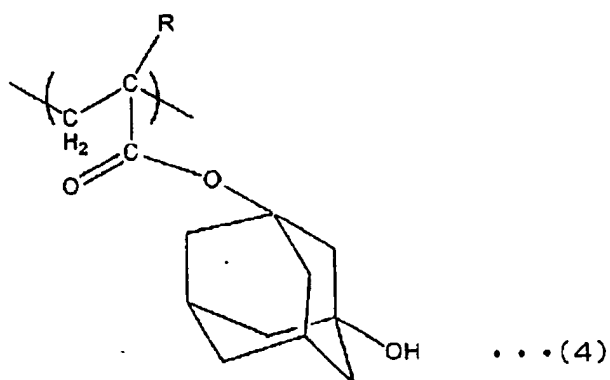
[Claim 4] The positive-resist constituent according to claim 1 to 3 whose unit (a2) is a unit guided from the acrylic ester containing a lactone content monocycloalkyl radical or a bicyclo alkyl group (meta).

[Claim 5] The positive-resist constituent according to claim 4 whose unit (a2) is a unit guided from the acrylic ester (meta) of gamma-butyrolactone.

[Claim 6] The positive-resist constituent according to claim 1 to 5 whose unit (a3) is a unit guided from the acrylic ester containing a hydroxyl-group content adamantyl radical (meta).

[Claim 7] The positive-resist constituent according to claim 6 whose unit (a3) is a unit expressed with the following general formula (4).

[Formula 4]



(The inside R of a formula is a hydrogen atom or a low-grade alkyl group)

[Claim 8] The positive-resist constituent according to claim 1 to 7 whose unit (a4) is a unit guided from at least one sort chosen from tricyclo deca nil (meta) acrylate, adamantyl (meta) acrylate, and tetracyclo dodecanyl (meta) acrylate.

[Claim 9] The positive-resist constituent according to claim 1 to 8 the 25-50-mol range of a unit (a1) is %, and the 25-50-mol range of whose unit (a2) is %, the 10-30-mol range of whose unit (a3) is % and the 5-25-mol range of whose unit (a4) is %.

[Claim 10] The positive-resist constituent according to claim 1 to 9 whose acid generator component (B) is onium salt which makes fluorination alkyl sulfonic-acid ion an anion.

[Claim 11] The positive-resist constituent according to claim 1 to 10 which comes to carry out 0.01-0.2 mass section combination of the second class low-grade fatty amine or the third class low-grade fatty amine (D) to a resinous principle (A).

[Claim 12] The formation approach of the resist pattern characterized by preparing a positive-resist constituent according to claim 1 to 11 on a substrate, giving exposure afterbaking for 40 - 120 seconds at 80-150 degrees C, and carrying out alkali development subsequently after giving prebake for 40 - 120 seconds and exposing it alternatively at 80-150 degrees C, and the ratio of the Rhine section size to tooth-space section size forming one or less resist pattern.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the chemistry magnification mold positive-resist constituent suitable for the process which uses wavelength, especially an ArF excimer laser 200nm or less as the light source, and the formation approach of a resist pattern of coming to use this.

[0002]

[Description of the Prior Art] Conventionally, what protected polyhydroxy styrene with the transparency high as a resinous principle of a chemistry magnification mold resist over a KrF excimer laser (248nm) and the hydroxyl group of this by the dissolution control radical of acid dissociation nature has been used. However, detailed-ization of a semiconductor device progresses increasingly and development of the process using an

ArF excimer laser (193nm) is furthered energetically by the end of today. In the process which makes an ArF excimer laser the light source, since the resin which has the benzene ring like polyhydroxy styrene has the inadequate transparency over an ArF excimer laser (193nm), using for this is unsuitable.

[0003] Therefore, without having the benzene ring, in order to solve such a fault, the resin which has the unit guided to the ester section which is excellent in dry etching-proof nature from acrylic ester with a polynuclear hydrocarbon radical like an adamantane frame or methacrylic ester in a principal chain attracts attention, and much proposals are made until now. (The patent No. 2881969 official report, JP,5-346668,A, JP,7-234511,A, JP,9-73173,A, JP,9-90637,A, JP,10-161313,A, JP,10-319595,A, and JP,11-12326,A) .

[0004] By the way, in semiconductor device manufacture, the resolution of narrowing, and a 150nm and near 100nm is further needed for the design rule needed, and the further improvement in resolution is demanded in recent years. Moreover, in addition to such improvement in definition, with the formation process of a resist pattern with which the ratio of resist line section size to tooth-space section size becomes that [one or less], the so-called formation of an isolated resist pattern with which the ratio of resist line section size to tooth-space section size is set to one ninth is needed, for example.

[0005]

[Problem(s) to be Solved by the Invention] However, in the conventional resist, there is a problem that the depth of focus width of face of such an isolated resist pattern is not enough, and the improvement is desired. Moreover, it is difficult for the isolated resist pattern section (non-dense pattern section), and an aforementioned line and an aforementioned tooth space to control such the proximity effect in the conventional resist, although the problem of the so-called proximity effect which a difference produces in the resist pattern size of the non-dense pattern section and the dense pattern section will arise in the formation process of a pattern with which the pattern section (dense pattern section) of 1:1 is intermingled, therefore the improvement is desired.

[0006] This invention was made in view of said situation, is excellent in definition, and aims at offering the formation approach of a chemistry magnification mold positive-resist constituent and the resist pattern using this which moreover enabled improvement in the depth of focus width of face of an isolated resist pattern, and control of the proximity effect.

[0007]

[Means for Solving the Problem] As a result of repeating research wholeheartedly that said object should be attained, by having the unit guided from the acrylic ester containing a specific 4 yuan copolymer (meta) in a principal chain, and using the resinous principle to which the solubility over alkali increases according to an operation of an acid as base resin, this invention persons found out that said object could be attained, and completed this invention.

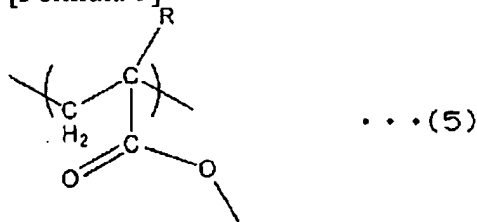
[0008] Namely, the positive-resist constituent of this invention The resinous principle to which it has the unit guided from acrylic ester in a principal chain, and the solubility over alkali increases according to an operation of an acid (A), (Meta) It is the positive-resist constituent which comes to dissolve the acid generator component (B) which generates an acid by exposure in an organic solvent (C). The unit guided from the acrylic ester in which a resinous principle (A) contains a polycyclic type machine content acid dissociation nature dissolution control radical (meta) (a1), The unit guided from the

acrylic ester containing a lactone content monocycle or a polycyclic type machine (meta) (a2), It is characterized by being a copolymer including the unit (a4) guided from the acrylic ester containing polycyclic type machines (meta) other than the unit (a3) guided from the acrylic ester containing a hydroxyl-group content polycyclic type machine (meta) and a unit (a1), a unit (a2), and a unit (a3).

[0009] Here with the unit guided from the aforementioned acrylic ester (meta) In the unit shown by the following general formula (5) in this description The unit guided from the acrylic ester whose R is hydrogen, the unit guided from the methacrylic ester whose R is a methyl group, Furthermore, R considers as the generic name of the low-grade alkyl group which are C2-about five C, and the unit which is specifically the alkyl group of the shape of a straight chain, such as an ethyl group, a propyl group, an isopropyl group, n-butyl, an isobutyl radical, tert-butyl, a pentyl radical, an isopentyl radical, and a neopentyl radical, and the letter of branching.

[0010]

[Formula 5]



[0011] Moreover, the formation approach of the resist pattern of this invention is characterized by preparing the aforementioned positive-resist constituent on a substrate, giving exposure afterbaking for 40 - 120 seconds at 80-150 degrees C, and carrying out alkali development subsequently, after giving prebake for 40 - 120 seconds and exposing it selectively at 80-150 degrees C, and the ratio of line section size to tooth-space section size forming one or less resist pattern.

[0012]

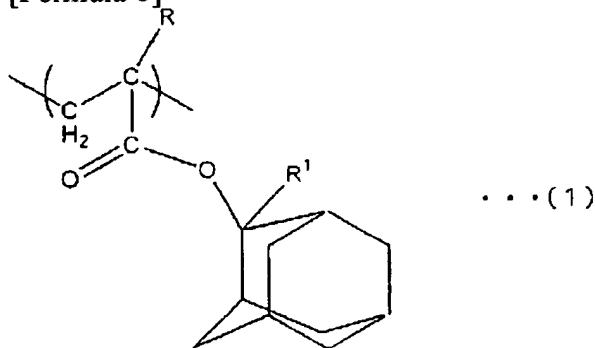
[Embodiment of the Invention] In the positive-resist constituent of this invention, it has the unit guided from acrylic ester (meta) in a principal chain as a resinous principle (A), and that to which the solubility over alkali increases according to an operation of an acid is used. That is, it has an acid dissociation nature dissolution control radical in this resinous principle (A), and when this radical dissociates with the acid generated from the acid generator, the resin which changes from alkali insolubility to alkali fusibility and in which alkali development is possible is used for it. By using such resin, when solubility [as opposed to alkali in the exposure section] increases, alkali fusibility is shown and an unexposed part maintains alkali insolubility.

[0013] When this resinous principle (A) is explained in full detail, this resinous principle (A) The unit guided from the acrylic ester containing a polycyclic type machine content acid dissociation nature dissolution control radical (meta) (a1), The unit guided from the acrylic ester containing a lactone content monocycle or a polycyclic type machine (meta) (a2), It is a copolymer including the unit (a4) guided from the acrylic ester containing polycyclic type machines (meta) other than the unit (a3) guided from the acrylic ester containing a hydroxyl-group content polycyclic type machine (meta) and these units (a1), a unit (a2), and a unit (a3). And by including each [these] unit (a1) - (a4), a resinous

[0014] A unit (a1) is a unit guided from the acrylic ester containing a polycyclic type machine content acid dissociation nature dissolution control radical (meta). As a polycyclic type machine, the radical excluding one hydrogen atom from the poly cycloalkanes, such as adamantane, norbornane, an iso bornane, tricyclodecane one, and a tetracyclo dodecane, is mentioned as a bicyclo alkane, a tricyclo alkane, TERORA cycloalkane, etc. Here, although many these were proposed in the ArF resist and can choose and use these polycyclic type machines for arbitration also in this invention, it is desirable to use an adamanthyl radical, a norbornyl radical, and a tetracyclo dodecanyl radical especially in respect of being easy to receive on industry etc.

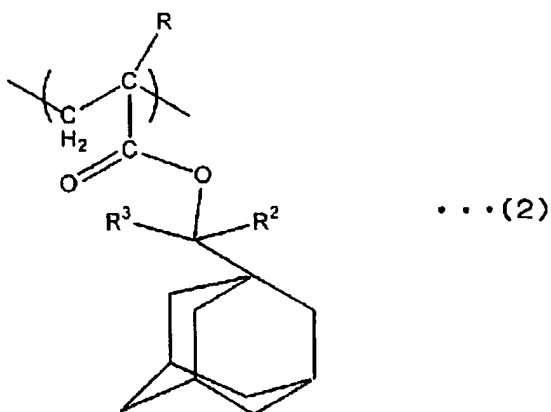
[0015] the acid dissociation nature dissolution control radical was mentioned above -- as -- before exposure -- the resinous principle (A) whole -- alkali -- it has the alkali dissolution control nature made insoluble, and dissociates according to an operation of the acid generated from the acid generator component (B) mentioned later after exposure, and the whole resinous principle (A) is changed to alkali fusibility. As such an acid dissociation nature dissolution control radical, what forms the 3rd class alkyl ester of the shape of the carboxyl group of an acrylic acid, annular, or a chain, for example (meta) is known widely. Although the thing of arbitration is usable, without being limited especially if it has the function mentioned above as a unit (a1), specifically, at least one sort chosen from the following general formula (1), (2), and (3) is desirable in respect of excelling in definition and dry etching-proof nature etc.

[Formula 6]



(For the inside R of a formula, a hydrogen atom or a low-grade alkyl group, and R1 are low-grade alkyl groups)

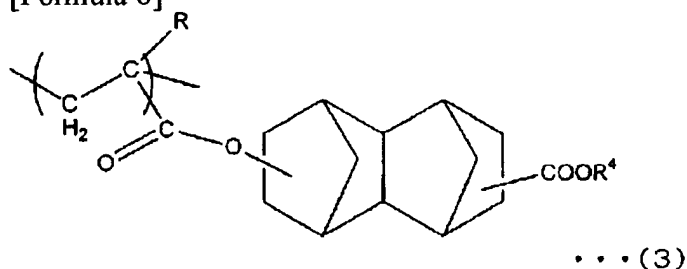
[Formula 7]



(For the inside R of a formula, a hydrogen atom or a low-grade alkyl group, R2, and R3 are low-grade alkyl groups independently, respectively)

[0018]

[Formula 8]



(For the inside R of a formula, a hydrogen atom or a low-grade alkyl group, and R4 are the 3rd class alkyl groups)

[0019] The unit expressed with a general formula (1) is the case where the carbon atom contiguous to the oxygen atom (-O-) of the ester section of an acrylic acid (meta) serves as the 3rd class alkyl group on a ring frame like an adamantanyl radical. as R -- a hydrogen atom or a methyl group -- further -- a C2-about five C low-grade alkyl group -- the alkyl group of the shape of a straight chain of low classes, such as an ethyl group, a propyl group, an isopropyl group, n-butyl, an isobutyl radical, tert-butyl, a pentyl radical, an isopentyl radical, and a neopentyl radical, and the letter of branching is specifically mentioned. Moreover, R1 If it carries out, the alkyl group of the shape of a straight chain of low classes, such as a methyl group, an ethyl group, a propyl group, an isopropyl group, n-butyl, an isobutyl radical, tert-butyl, a pentyl radical, an isopentyl radical, and a neopentyl radical, and the letter of branching is mentioned. Here, it is R1. It is in the inclination for acid dissociation nature to become high compared with the case of a with a carbon numbers of two or more alkyl group, then a methyl group and is desirable. However, considering as a methyl group industrially is most desirable.

[0020] The carbon atom contiguous to the oxygen atom (-O-) of the ester section of an acrylic acid (meta) is the 3rd class alkyl group, and the unit expressed with a general formula (2) is the case where a ring frame still like an adamantanyl radical exists in this alkyl group. In the unit expressed with a general formula (2), R is the same definition as the case of said general formula (1), and it is R2. And R3 They are the low-grade alkyl group which became independent, respectively, i.e., the above mentioned shape of a C1-

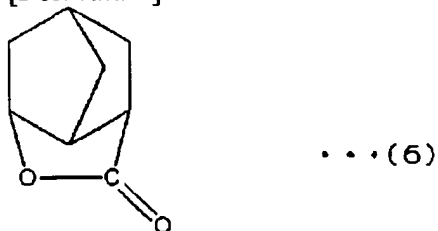
about five C straight chain, and a letter alkyl group of branching. As for such a radical, acid dissociation nature tends to become high from a 2-methyl-2-adamantyl radical. In addition, above R2 And R3 If it attaches, considering as both methyl groups is industrially desirable.

[0021] The carbon atom contiguous to the oxygen atom (-O-) of another ester section instead of the acrylic ester (meta) section is the 3rd class alkyl group, and the unit expressed with a general formula (3) is the case where this ester section and the acrylic ester (meta) section are connected by ring frame like a tetracyclo dodecanyl radical. In the unit expressed with a general formula (3), R is the same definition as the case of said general formula (1), and it is R4. It is the 3rd class alkyl group like tert-butyl or a tert-amyl group. In addition, R4 If it attaches, considering as tert-butyl is industrially desirable. Moreover, especially in the unit expressed with such general formula (1) - (3), it is the unit expressed with a general formula (1), and is R1. What is a methyl group or an ethyl group is desirable in respect of excelling in definition etc.

[0022] A unit (a2) is a unit guided from the acrylic ester containing a lactone content monocycle or a polycyclic type machine (meta). A lactone functional group is effective, when raising the adhesion to the substrate of the resist film formed from the constituent of this invention or raising a hydrophilic property with a developer. As [both] a unit (a2), especially if it has such a lactone functional group and a ring machine, the thing of arbitration is usable, without being limited. The radical excluding one hydrogen atom from the bicyclo alkane which the radical excluding one hydrogen atom from gamma-butyrolactone is mentioned as a lactone content monocycle type machine, and specifically has a lactone radical as a lactone content polycyclic type machine, the tricyclo alkane, and the tetracyclo alkane is mentioned. It is advantageous in respect of the radical excluding the hydrogen atom from the lactone content bicyclo alkane which has the following structure expressions (6) especially, or the tricyclo alkane which has a structure expression (7) tending to receive one on industry etc.

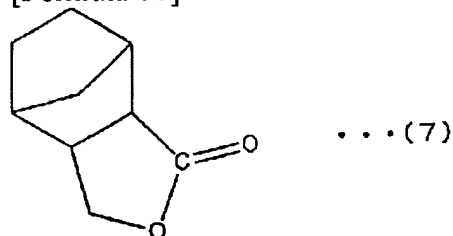
[0023]

[Formula 9]



[0024]

[Formula 10]

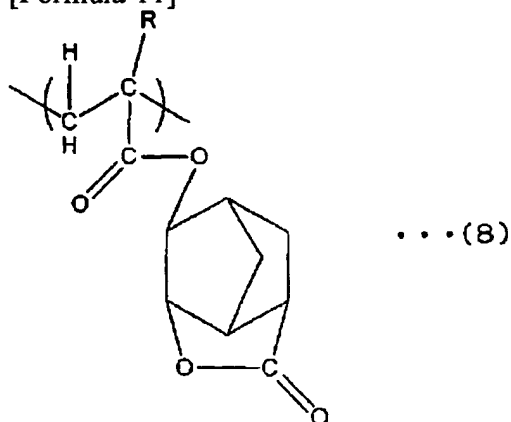


[0025] Moreover, specifically, the unit expressed with following general formula (8) -

(10) guided from the acrylic ester containing a lactone content monocycloalkyl radical or a bicyclo alkyl group (meta) is mentioned as a unit (a2).

[0026]

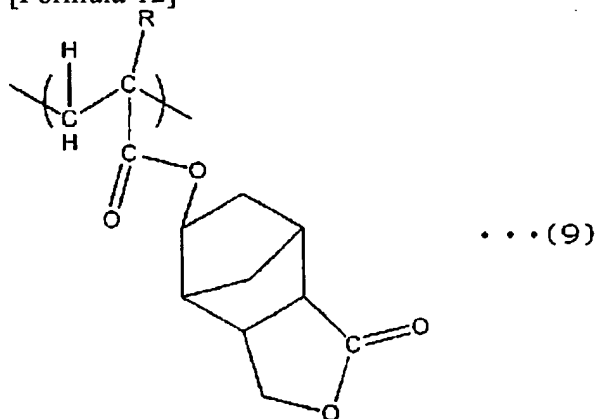
[Formula 11]



(The inside R of a formula is a hydrogen atom or a low-grade alkyl group)

[0027]

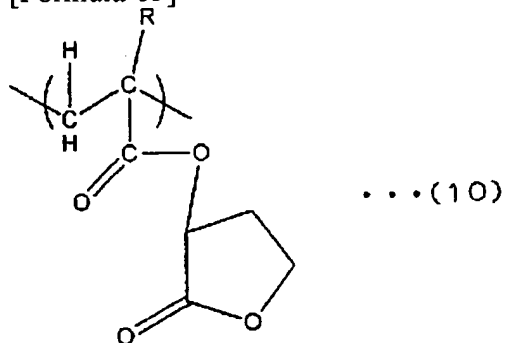
[Formula 12]



(The inside R of a formula is a hydrogen atom or a low-grade alkyl group)

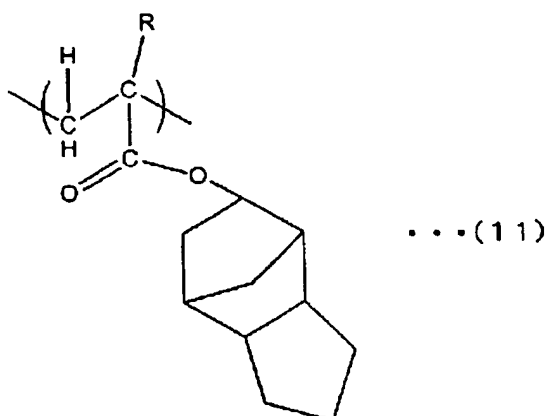
[0028]

[Formula 13]



(The inside R of a formula is a hydrogen atom or a low-grade alkyl group)

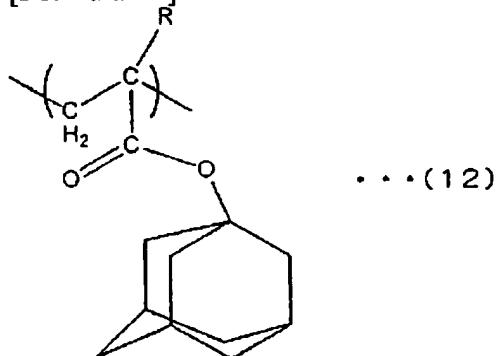
[0029] Moreover, especially in the unit expressed with such general formula (8) - (10),



(The inside R of a formula is a hydrogen atom or a low-grade alkyl group)

[0034]

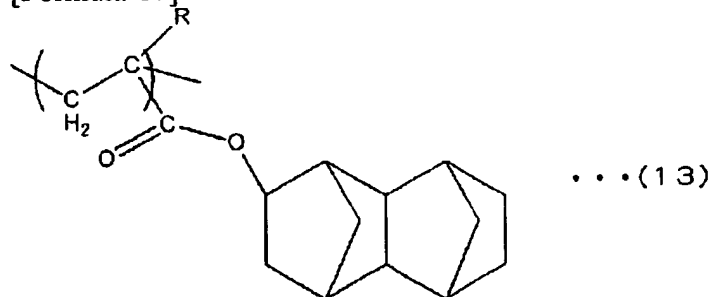
[Formula 16]



(The inside R of a formula is a hydrogen atom or a low-grade alkyl group)

[0035]

[Formula 17]



(The inside R of a formula is a hydrogen atom or a low-grade alkyl group)

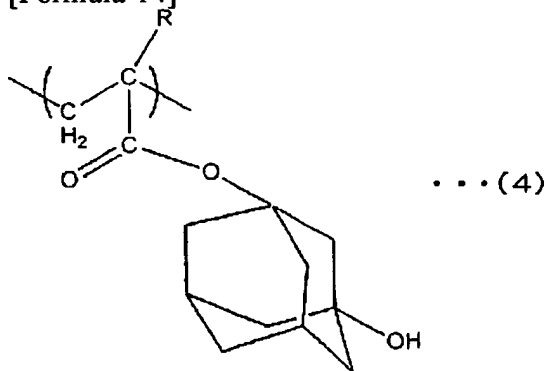
[0036] Here about each unit (a1) in a resinous principle (A) - (a4) a rate It is the 30-40-mol range of % preferably. a unit (a1) -- 25-50-mol % -- a unit (a2) -- 25-50-mol % -- desirable -- the 30-40-mol range of % -- it is -- a unit (a3) -- 10-30-mol % -- it is the 10-20-mol range of % preferably, and a unit (a4) is made suitable [5-25 mol % and a thing / the 10-20 mol range of % / preferably]. The depth of focus width of face of such range, then the isolated pattern formed from the resist constituent obtained can be raised greatly, and the proximity effect can also fully be controlled, and this can be reduced greatly. In addition, when it deviates from the aforementioned range greatly, there is a possibility

the unit guided from the gamma-butyrolactone ester of the acrylic acid which has an ester bond to alpha carbon (meta) (meta), i.e., the acrylic ester of gamma-butyrolactone, is desirable in respect of the effectiveness about control and reduction of the proximity effect being excellent etc.

[0030] A unit (a3) is a unit guided from the acrylic ester containing a hydroxyl-group content polycyclic type machine (meta), by having the hydroxyl group which is a polar group, it raises a hydrophilic property with the developer of the whole resinous principle (A), improves the alkali solubility of the exposure section, and, thereby, contributes to improvement in definition. Here, as a polycyclic type machine, the same polycyclic type machine as the case of the aforementioned unit (a1) can be used. The thing of arbitration is usable, without being limited as such a unit (a3), especially if it is a hydroxyl-group content polycyclic type machine. Specifically, a hydroxyl-group content adamantyl radical, especially the unit expressed with the following general formula (4) are desirable at the point of having the effectiveness of raising dry etching-proof nature, and the effectiveness which makes a pattern cross section the shape of a rectangle.

[0031]

[Formula 14]



(The inside R of a formula is a hydrogen atom or a low-grade alkyl group)

[0032] (a4) A unit is a unit guided from the acrylic ester containing polycyclic type machines (meta) other than the aforementioned unit (a1), a unit (a2), and a unit (a3). Here, semantics other than a unit (a1), a unit (a2), and a unit (a3) means that these are not overlapped, namely, means holding no radicals, such as an acid dissociation nature dissolution control radical in a unit (a1), a lactone radical in a unit (a2), and a hydroxyl group in a unit (a3). Moreover, as a polycyclic type machine, the same polycyclic type machine as the case of the aforementioned unit (a1) can be used. Although the thing of a large number known from the former as an ArF POJIREJISUTO ingredient is usable as a unit (a4) which comes to have such a polycyclic type machine, the unit guided from at least one sort especially chosen from tricyclo deca nil (meta) acrylate, adamantyl (meta) acrylate, and tetracyclo dodecanyl (meta) acrylate is desirable in respect of being easy to receive on industry etc. In addition, these illustrated units are shown as general formula (11) - (13) below.

[0033]

[Formula 15]

that the nonconformity that definition falls may arise.

[0037] In the resist constituent of this invention moreover, as a resinous principle (A) The acrylic-acid derivative which has a dry etching-proof disposition top radical well-known as a positive resist of a chemistry magnification mold, and a **** dissociative dissolution control radical conventionally in the monomer which forms each aforementioned unit (a1) - (a4), The carboxylic acid which has an ethylene nature double bond for considering as alkali fusibility, such as a methacrylic-acid derivative, an acrylic acid, a methacrylic acid, a maleic acid, and a fumaric acid, If needed, the well-known monomer used for manufacture of acrylic resin is combined suitably, and can carry out copolymerization, and it can also use.

[0038] As the aforementioned acrylic-acid derivative, the acrylic ester which protected the hydroxyl group of carboxyl groups, such as ester of acrylic-acid naphthyl, acrylic-acid benzyl, acrylic-acid 3-oxocyclohexyl, an acrylic acid, and a terpeneol and ester of an acrylic acid and 3-bromoacetone, by the dry etching-proof disposition top radical or the **** dissociative substituent, for example is mentioned. Moreover, as a methacrylic-acid derivative, the derivative of the methacrylic acid corresponding to these acrylic-acid derivatives can be mentioned.

[0039] Moreover, as a carboxylic acid which has an ethylene nature double bond, an acrylic acid, a methacrylic acid, a maleic acid, a fumaric acid, etc. are mentioned, for example. As an example of the well-known monomer used for manufacture of acrylic resin, acrylic-acid alkyl ester, corresponding alkyl methacrylate ester, etc., such as a methyl acrylate, an ethyl acrylate, acrylic-acid propyl, acrylic-acid isopropyl, acrylic-acid n-butyl, isobutyl acrylate, acrylic-acid n-hexyl, acrylic-acid octyl, 2-ethylhexyl acrylate, acrylic-acid lauryl, acrylic-acid 2-hydroxyethyl, and 2-hydroxypropyl acrylate, can be mentioned, for example.

[0040] In addition, about a resinous principle (A), a corresponding (meta) acrylic ester monomer is made [manufacturing easily or] by the well-known radical polymerization using a radical polymerization initiator like azobisisobutyronitril (azobisisobutyronitrile) etc. Moreover, about the weight average molecular weight of a resinous principle (A), it is still more desirable that making it the range of 5000-20000 makes it preferably the range of 8000-15000.

[0041] In the resist constituent of this invention, out of a thing conventionally well-known as an acid generator in a chemistry magnification mold resist as an acid generator component (B) which generates an acid by exposure, the thing of arbitration can be chosen suitably and can be used. As this acid generator, for example Diphenyliodonium trifluoromethane sulfonate, Phenyliodonium trifluoromethane sulfonate, (4-methoxyphenyl) Bis(p-tert-buthylphenyl) iodonium trifluoromethane sulfonate, Triphenylsulfonium trifluoromethane sulfonate, diphenyl (4-methoxyphenyl) sulfonium trifluoromethane sulfonate, Diphenyl sulfonium trifluoromethane sulfonate, (p-tert-buthylphenyl) Diphenyliodonium nonafluorobutane sulfonate, bis(p-tert-buthylphenyl) iodonium nonafluorobutane sulfonate, Onium salt, such as triphenylsulfonium nonafluorobutane sulfonate, is used and the onium salt which makes fluorination alkyl sulfonic-acid ion an anion especially is used suitably.

[0042] As such an acid generator component (B), one sort may be used independently and you may use combining two or more sorts. About the loadings, it is desirable to consider as the range of 0.5 - 30 mass section to the (resinous principle A) 100 mass

section, and it is more desirable to consider as the range of 1 - 10 mass section. When there is a possibility that pattern formation may no longer be made for loadings fully under in the 0.5 mass section and 30 mass sections are exceeded, there is a possibility that a uniform solution may become is hard to be obtained, and preservation stability may fall. [0043] Moreover, an aforementioned resinous principle (A) and an aforementioned acid generator component (B) are dissolved in an organic solvent (C), and let the positive-resist constituent of this invention be a solution. what can dissolve both the aforementioned components and can be used as a uniform solution as an organic solvent (C) used -- it is -- ****ing -- the thing of the arbitration out of a thing conventionally well-known as a solvent of a chemistry magnification mold resist -- one sort -- or it can choose suitably and two or more sorts can be used.

[0044] As such an organic solvent (C), for example An acetone, a methyl ethyl ketone, Ketones, such as a cyclohexanone, methyl isoamyl ketone, and 2-heptanone Ethylene glycol and ethylene glycol mono-acetate, a diethylene glycol, Diethylene-glycol mono-acetate, propylene glycol, and propylene glycol mono-acetate, The monomethyl ether of dipropylene glycol or dipropylene glycol mono-acetate, Polyhydric alcohol, such as the monoethyl ether, the monopropyl ether, the monobutyl ether, or the monophenyl ether, and the derivative of those, Ester, such as ring type ether like dioxane, methyl lactate, ethyl lactate, methyl acetate and ethyl acetate, butyl acetate, methyl pyruvate, pyruvic-acid ethyl, methoxy methyl propionate, and ethoxy ethyl propionate, can be mentioned.

[0045] In addition, it is desirable to use the partially aromatic solvent of at least one sort chosen from propylene-glycol-monomethyl-ether acetate and ethyl lactate and gamma-PUCHIRO lactone especially as this organic solvent (C). In that case, it is desirable to choose as a mixed rate, so that the mass ratio of the former and the latter may serve as the range of 70:30 thru/or 97:3.

[0046] Moreover, a resist pattern configuration and since it lengthens and places and stability with the passage of time etc. is raised, the second class low-grade fatty amine or the third class low-grade fatty amine (D) can be made to contain as still more nearly another component in the resist constituent of this invention. As this the second class or third class low-grade fatty amine (D), although a trimethylamine, diethylamine, triethylamine, G n propylamine, tree n propylamine, tripentylamine, diethanolamine, triethanolamine, etc. are mentioned, for example, especially a thoria RUKANORU amine is desirable. These may be used independently and may be used combining two or more sorts. To the aforementioned resinous principle (A), such an amine (D) is usually blended in the range of the 0.01 - 0.2 mass section, and is used.

[0047] Moreover, in the resist constituent of this invention, addition content of the surfactant for raising the additional resin for improving the engine performance of the additive which has a miscibility if needed further, for example, the resist film, and spreading nature, a dissolution inhibitor, a plasticizer, a stabilizer, a coloring agent, the antihalation agent, etc. can be carried out.

[0048] Next, the formation approach of the resist pattern of this invention is explained as an example of the operation of the positive-resist constituent of such this invention. In addition, to one or less resist pattern, the ratio of line section size to tooth-space section size shall be an effective approach, and shall apply especially this approach to formation of such a pattern also in this example. First, the positive-resist constituent of this invention is applied on the substrate which consists of a silicon wafer etc. Conventional

methods, such as a spin coat method, are adopted as the method of application. Next, the applied constituent is heated for 40 - 120 seconds at 80-150 degrees C, prebake is given, and it considers as a sensitization layer. Subsequently, for example with an ArF aligner, ArF excimer laser light is irradiated through a desired mask pattern at said sensitization layer, and it exposes selectively. Then, the exposed sensitization layer is heated for 40 - 120 seconds at 80-150 degrees C, and exposure afterbaking (PEB) is given. Then, the development of this is carried out using an alkali developer, for example, a 0.1 - 10 mass % tetramethylammonium hydroxide water solution. Thus, the ratio of line section size to a pattern faithful to a mask pattern, especially tooth-space section size can obtain one or less resist pattern.

[0049] In addition, although especially the resist constituent of this invention is effective when an ArF excimer laser is used as a source of exposure, it is more effective than it also to radiations, such as F2 laser of short wavelength, EUV (extreme ultraviolet rays) and VUV (vacuum ultraviolet radiation), an electron ray, an X-ray, and soft X ray.

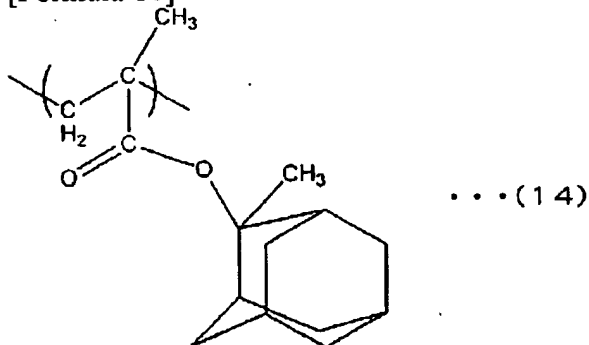
[0050]

[Example] Hereafter, an example explains this invention still more concretely.

(Example 1) 100 mass sections preparation of the copolymer of each unit expressed with following structure-expression (14) - (17) was first carried out as a resinous principle (A). Structure expression (14) The unit expressed with 15-mol % and a structure expression (17) in the unit expressed with 35-mol % and a structure expression (16) as a rate in the copolymer of each unit expressed with - (17) in the unit expressed with 35-mol % and a structure expression (15) in the unit expressed with a structure expression (14) was made into 15-mol %. In addition, weight average molecular weight of this copolymer was set to 10000.

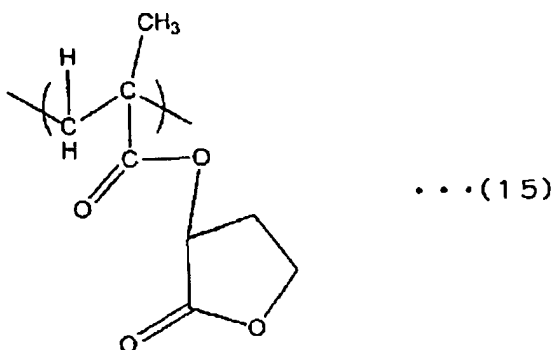
[0051]

[Formula 18]



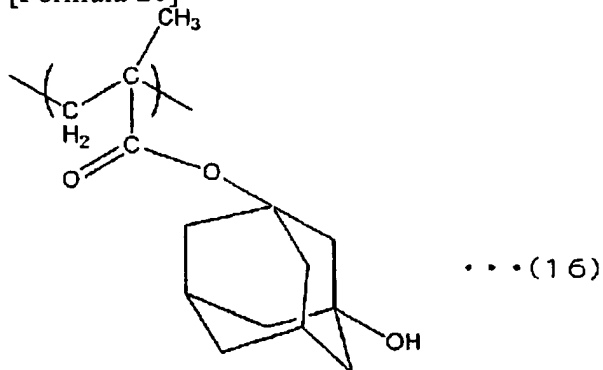
[0052]

[Formula 19]



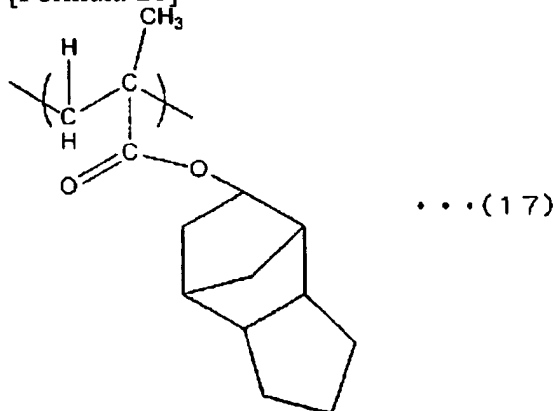
[0053]

[Formula 20]



[0054]

[Formula 21]



[0055] Moreover, 2 mass sections preparation of the triphenyl SURUHONIMU nonafluorobutane sulfonate was carried out as an acid generator component (B), 0.2 mass section preparation of the triethanolamine was carried out as third class low-grade fatty amine (D), and the mixed solvent which consists of the propylene-glycol-monomethyl-ether acetate 750 mass section and the gamma-butyrolactone 30 mass section as an organic solvent (C) further was prepared. Next, the prepared resinous principle (A), an acid generator component (B), and fatty amine (D) were altogether dissolved in said organic solvent (C), and the uniform positive-resist solution (constituent) used as the example 1 of this invention was obtained.

[0056] Subsequently, the resist layer of 350nm of thickness was formed by applying this resist solution on a silicon wafer using a spinner, and carrying out stoving (pre bake) for 90 seconds at 125 degrees C on a hot plate. With subsequently, the ArF aligner (ISI company make, "trade name MICRO STEP"; NA=0.60, sigma=0.75)", exposure afterbaking (PEB) processing for 90 seconds was continuously irradiated selectively and performed at 125 degrees C in order to form in a pattern which mentions ArF excimer laser light (193nm) later. Subsequently, paddle development was carried out for 60 seconds in the tetramethylammonium hydroxide water solution of 2.38 mass % in 23 degrees C, and after that, it rinsed for 20 seconds and dried.

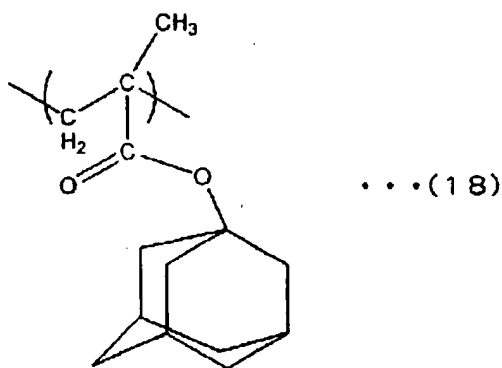
[0057] The isolated resist pattern formed among the resist patterns formed of such actuation of a 120nm resist line pattern and tooth-space 1080nm (1:9) was formed in the good configuration, and the depth of focus width of face was 500nm. Moreover, the variation of tolerance of the 120nm line and tooth-space pattern (1:1) which are another pattern, and said isolated resist pattern is 50nm, and it turned out that the proximity effect is small enough. Moreover, it was 7.6nm when asked for 3sigma which is the scale which shows LER (line edge roughness) about this 120nm line and a tooth-space pattern (1:1). Furthermore, when asked for whenever [exposure allowances / which this 120nm line and a tooth-space pattern (1:1) can form in plus minus 10% error range], it was 10.8% of the pin center, large light exposure from which this line and a tooth-space pattern are obtained.

[0058] In addition, above LER (line edge roughness) means the uneven irregularity formed in the side attachment wall of a line and a tooth-space pattern in the resist pattern after development. Moreover, 3sigma used as the scale of this has so little irregularity that the value is small, and becoming a good pattern is shown. Moreover, whenever [exposure allowances] (exposure margin) is defined as follows. although light exposure required to form the resist pattern size made into a certain object is boiled to some extent and decided, on a real substrate, it may be influenced of a level difference etc. and light exposure may change Thus, even if the once regular light exposure shifts to some extent, it is called exposure margin (whenever [exposure allowances]) that the target resist pattern is obtained. The larger (large) one of this numeric value is good.

[0059] (Example 2) As a resinous principle (A), it used as it is about each unit of the structure expression (14) in an example 1, a structure expression (15), and a structure expression (16), and it replaced with the unit of a structure expression (17), the copolymer using the unit of the following structure expression (18) was manufactured, and 100 mass sections preparation of this was carried out. In addition, as a rate in the copolymer of each unit, it presupposed that it is the same as an example 1 about each unit of a structure expression (14), a structure expression (15), and a structure expression (16), and it was presupposed about the unit of a structure expression (18) that it is the same as the rate of the unit of the structure expression (17) in an example 1. Moreover, weight average molecular weight of this copolymer was also set to 10000. Moreover, except this resinous principle (A), the uniform positive-resist solution (constituent) used as the example 2 of this invention was obtained by making it the same as an example 1. Subsequently, it processed like the example 1 using this resist solution, and the resist pattern was formed.

[0060]

[Formula 22]

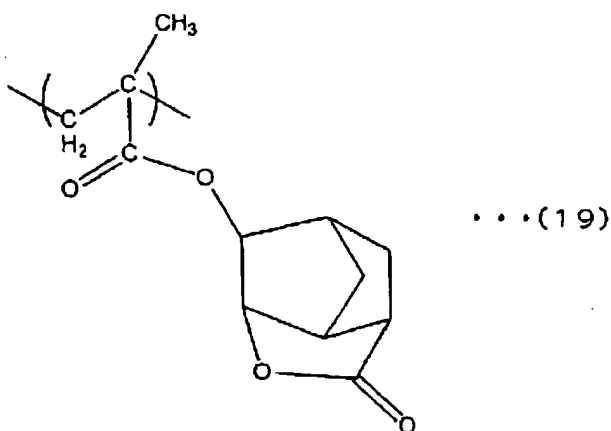


[0061] The isolated resist pattern formed among the resist patterns formed of such actuation of a 120nm resist line pattern and tooth-space 1080nm (1:9) was formed in the good configuration, and the depth of focus width of face was 600nm. Moreover, the variation of tolerance of the 120nm line and tooth-space pattern (1:1) which are another pattern, and said isolated resist pattern is 45nm, and it turned out that the proximity effect is small enough. Moreover, it was 8.3nm when asked for 3sigma which is the scale which shows LER (line edge roughness) about this 120nm line and a tooth-space pattern (1:1). Furthermore, when asked for whenever [exposure allowances / which this 120nm line and a tooth-space pattern (1:1) can form in plus minus 10% error range], it was 11.4% of the pin center, large light exposure from which this line and a tooth-space pattern are obtained.

[0062] (Example 3) As a resinous principle (A), it used as it is about each unit of the structure expression (14) in an example 2, a structure expression (16), and a structure expression (18), and it replaced with the unit of a structure expression (15), the copolymer using the unit of the following structure expression (19) was manufactured, and 100 mass sections preparation of this was carried out. In addition, as a rate in the copolymer of each unit, it presupposed that it is the same as an example 2 about each unit of a structure expression (14), a structure expression (16), and a structure expression (18), and it was presupposed about the unit of a structure expression (19) that it is the same as the rate of the unit of the structure expression (15) in an example 2. Moreover, weight average molecular weight of this copolymer was also set to 10000. Moreover, except this resinous principle (A), the uniform positive-resist solution (constituent) used as the example 3 of this invention was obtained by making it the same as an example 1. Subsequently, it processed like the example 1 using this resist solution, and the resist pattern was formed.

[0063]

[Formula 23]



[0064] The isolated resist pattern formed among the resist patterns formed of such actuation of a 120nm resist line pattern and tooth-space 1080nm (1:9) was formed in the good configuration, and the depth of focus width of face was 600nm. Moreover, the variation of tolerance of the 120nm line and tooth-space pattern (1:1) which are another pattern, and said isolated resist pattern is 50nm, and it turned out that the proximity effect is small enough. Moreover, it was 6.5nm when asked for 3sigma which is the scale which shows LER (line edge roughness) about this 120nm line and a tooth-space pattern (1:1). Furthermore, when asked for whenever [exposure allowances / which this 120nm line and a tooth-space pattern (1:1) can form in plus minus 10% error range], it was 9.2% of the pin center, large light exposure from which this line and a tooth-space pattern are obtained.

[0065] (Example 1 of a comparison) Using as it is as a resinous principle (A) about each unit of the structure expression (14) in an example 1, a structure expression (15), and a structure expression (16), the unit of a structure expression (17) manufactured the copolymer, without using, and carried out 100-mass sections preparation of this. In addition, the unit expressed with 40-mol % and a structure expression (16) as a rate in the copolymer of each unit in the unit expressed with 40-mol % and a structure expression (15) in the unit expressed with a structure expression (14) was made into 20-mol %. Moreover, weight average molecular weight of this copolymer was also set to 10000. Moreover, except this resinous principle (A), the uniform positive-resist solution (constituent) used as the example 1 of a comparison was obtained by making it the same as an example 1. Subsequently, it processed like the example 1 using this resist solution, and the resist pattern was formed.

[0066] Although the isolated resist pattern formed among the resist patterns formed of such actuation of a 120nm resist line pattern and tooth-space 1080nm (1:9) was formed in the good configuration, the depth of focus width of face was 400nm. Moreover, the variation of tolerance of the 120nm line and tooth-space pattern (1:1) which are another pattern, and said isolated resist pattern is 45nm, and the proximity effect was small. Moreover, it was 11.3nm when asked for 3sigma which is the scale which shows LER (line edge roughness) about this 120nm line and a tooth-space pattern (1:1). Furthermore, when asked for whenever [exposure allowances / which this 120nm line and a tooth-space pattern (1:1) can form in plus minus 10% error range], it was 9.1% of the pin center, large light exposure from which this line and a tooth-space pattern are obtained.

[0067] (Example 2 of a comparison) Using as it is as a resinous principle (A) about each

unit of the structure expression (14) in an example 1, a structure expression (15), and a structure expression (16), the unit of a structure expression (17) manufactured the copolymer, without using, and carried out 100 mass sections preparation of this. In addition, the unit expressed with 35-mol % and a structure expression (16) as a rate in the copolymer of each unit in the unit expressed with 35-mol % and a structure expression (15) in the unit expressed with a structure expression (14) was made into 30-mol %. Moreover, weight average molecular weight of this copolymer was also set to 10000. Moreover, as an organic solvent (C), it replaced with the thing of an example 1 and the mixed solvent which consists of the ethyl lactate 750 mass section and the gamma-butyrolactone 30 mass section was prepared. About except [these], the uniform positive-resist solution (constituent) used as the example 2 of a comparison was obtained by making it the same as an example 1. Subsequently, it processed like the example 1 using this resist solution, and the resist pattern was formed.

[0068] Although the isolated resist pattern formed among the resist patterns formed of such actuation of a 120nm resist line pattern and tooth-space 1080nm (1:9) was formed in the good configuration, the depth of focus width of face was 300nm. Moreover, the variation of tolerance of the 120nm line and tooth-space pattern (1:1) which are another pattern, and said isolated resist pattern is 60nm, and the proximity effect did not become small. Moreover, it was 8.3nm when asked for 3sigma which is the scale which shows LER (line edge roughness) about this 120nm line and a tooth-space pattern (1:1). Furthermore, when asked for whenever [exposure allowances / which this 120nm line and a tooth-space pattern (1:1) can form in plus minus 10% error range], it was 8.8% of the pin center, large light exposure from which this line and a tooth-space pattern are obtained.

[0069] The above result is shown collectively below.

Depth of focus width of face Variation of tolerance 3sigma Whenever [exposure allowances] [nm] [nm] [nm] [%]

An example 1 500 50 7.6 10.8 Example 2 600 45 8.3 11.4 Example 3 600 50 6.5 9.2 The example 1 of a comparison 400 45 11.3 9.1 The example 2 of a comparison 300 60 8.3 From the result of 8.8 or more, especially the examples 1-3 of this invention are excellent in the depth of focus width of face of an isolated resist pattern, and since the variation of tolerance between patterns is also small, there is effectiveness also in reduction of the proximity effect, and excelling in definition was checked. Moreover, it turned out that the examples 1-3 of this invention are excellent also in also whenever [LER (line edge roughness) or exposure allowances].

[0070]

[Effect of the Invention] As explained above, the positive-resist constituent of this invention It has the unit guided from the acrylic ester containing a specific 4 yuan copolymer (meta) in a principal chain. Since the resinous principle to which the solubility over alkali increases according to an operation of an acid is used as base resin While becoming what was excellent in definition when a response in ArF excimer laser light was attained and improving the depth of focus width of face of an isolated resist pattern moreover, it becomes the chemistry magnification mold positive-resist constituent which can control the proximity effect and can reduce this. Moreover, this positive-resist constituent also does so the effectiveness that LER (line edge roughness) can be reduced in addition to the aforementioned effectiveness, and the effectiveness that an exposure

margin (whenever [exposure allowances]) becomes large. Therefore, this positive-resist constituent is used suitable for manufacture of the semiconductor device as which micro-machining is required as a positive resist of the chemistry magnification mold which makes ArF excimer laser light the light source.

[0071] Moreover, when the formation approach of the resist pattern of this invention uses the aforementioned positive-resist constituent, the ratio of line section size especially to tooth-space section size serves as an effective approach to one or less resist pattern.
